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1. PRELIMINARY NOTE

ON

The Chemistry of Concrete Otto of Boronia megastigma (Nees)

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Although the Concrete Otto of Boronia megastigma is a well-known article of commerce, practically no information is available regarding its chemical composition. It was with this objective in view that the writer commenced its examination in 1924. Since that date a very interesting account of this rutaceous plant from West Australia, together with notes regarding the preparation of the Concrete and some constants on the green oil separated from the extractive, appeared in the "Australasian Journal of Pharmacy," 20th October, 1926, pages 932-934. It was based upon a paper entitled "Work on Perfumes and Essential Oils done in West Australia," by Mr. W. B. Garner, contributed to the Australasian Pharmaceutical Conference held in Perth, W.A., in August, 1926.

The quantity of the Concrete Otto available for experimental purposes was naturally very limited, and its examination could not have been attempted had it not been for the courteous assistance rendered by Messrs. Plaimar Limited, Perth, W.A., in furnishing five ounces of the Concrete at cost price. On account of the large percentage of Triacontane present even this quantity failed to suffice, especially as the cost of further supplies proved prohibitive to the Institution to which I am attached. Mr. R. B. Scammell, B.Sc., of Messrs. F. H. Faulding & Co., Limited, Sydney, kindly overcame the difficulty and rendered invaluable assistance by furnishing several ounces in 1926 free of cost. This very generous donation was greatly appreciated, and the opportunity is availed of to express thanks for the gift.

The examination is naturally somewhat incomplete, but in view of the commercial importance of this Boronia Concrete in perfumery, the time is considered opportune for the publication of whatever information is available to pave the way for a more extensive investigation on much larger quantities of material. If any of the West Australian manufacturers should feel disposed to make available a quantity for further investigation, I shall be very pleased to undertake its examination.

EXPERIMENTAL.

The Concrete Otto of Boronia megastigma.

The samples received were of a greenish colour and butter-like consistency, possessing the powerful and characteristic odour of the flowers of the plant. The colouring matter, of course, was due to chlorophyll. The constituents which have so far been indentified are Triacontane (a paraffin of melting point 64°), a glyceride of palmitic and stearic acids, Phytosterols, free palmitic, formic, and caprylic acids with small quantities of ethylalcohol and ethyl formate, and unidentified phenolic bodies. These constituents undoubtedly form an excellent fixative or carrier for the odoriferous components eonsisting of an unidentified alcohol and probably β -Ionone.

The various samples of Concrete Otto, as received, gave the following

chemical and physical constants, as shown in Table:-

Date.	Melt- ing Point,	d15° 15	n D	Acid No.	Acid No. plus Ester No.	Ester No. after Acetyla- tion.	Source.
3/11/1924	35-36°	15° 0.8989	1.4752 (38°) 27·	106.7	139 · 5	Plaimar, Ltd. Perth, W.A.
26/10/1926	40°	40° 0.9091 15	1.4826 (40°) 24·5	95.9	136.5	do.
10 /2 /1927 (1925 product)	40 /41°	40° 0.9189 15	1.4842 (39°) 22·8	3 109.3	149.0	F. H. Faulding & Co. Ltd., Sydney.
10 /2/1927 (1926 product)	39/40°	40° 0.9173 15	1.4852 (38°) 30 · (5 107.3	147.8	do.

The best method of examination was found to be as follows:—40-grams of the Concrete Otto were dissolved in 200 c.c. absolute alcohol by warming on a steam bath and the solution allowed to stand during the week-end for the precipitation of the paraffin. The solution was then cooled to 15°, and the paraffin pumped off on to Buchner filter funnel. Six grams crude paraffin were thus obtained. The alcohol was removed from the filtrate by distillation under reduced pressure, whilst any further small quantities of paraffin which separated were removed by filtration. The residue was dissolved in ether and treated with 8% sodium hydroxide solution for the removal of free acids and phenolic bodies. The weight obtained was 4·5 grams. The ether was distilled off and the residue treated with alcoholic potash solution to decompose the esters and glycerides present. The small quantity of oil thus recovered was subjected to distillation at 2-3 mm.

Determination of Triacontane.—The various samples of crude paraffin were purified by re-crystallisation from boiling acetone when a final melting point of 64° was attained. It was definitely identified as Triacontane by combustion and molecular weight determinations.

(a)
$$0.1148$$
 gram gave on combustion 0.3590 gram CO_2 and 0.1546 gram H_2O .

$$C = 85.29\%$$

$$H = 15.00\%$$

$$C_{30} H_{62}$$
 requires $C = 85.30\%$

$$H = 14.70\%$$

(b) 0.9664 gram in 20 c.c. acetone elevated the boiling point 0.25° . M Wt = 429. C_{30} H₆₂ requires 422.

Determination of Glyceride.—The liquors from the hot alcoholic potash saponification were decomposed with dilute sulphuric acid and the combined fatty acids so liberated were re-crystallised from alcohol. They melted at 55-57° and possessed a mean molecular weight of 279.

The quantity, 9 grams, was altogether too small for identification, but experience with mixed glycerides from other sources leads one to tentatively class the acids as a mixture of stearic and palmitic. Glycerine was detected in the liquors, after removal of the fatty acids by filtration and volatile acids by steam distillation, by evaporation to dryness and extraction of the residue with a mixture of alcohol and ether. The residue after removal of solvent was confirmed as Glycerol by all qualitative tests, especially the Acrolein reaction.

Determination of Combined Volatile Acids.—The filtrate from the solid fatty acids yielded a small quantity of volatile acid on steam distillation. The ammonium salt gave the qualitative reactions for formic acid, whilst the silver salt prepared therefrom by its chemical deportment confirmed same. 0.1062 gram of silver salt on ignition gave 0.0792 gram silver equalling 74.57%. (The slightly high result was due to contamination with reduced silver.)

Determination of Free Acids.—The mixture of crude acid and phenols, being semi-solid, was placed on a porous tile for the absorption of the liquid phenol. The solid portion, on purification from methyl alcohol, melted at 62°. Combustion and molecular weight determinations offered confirmation of its identity with palmitic acid. A mixed melting point determination made with a sample of the acid from another source showed no depression.

Another sample of crude acid and phenol showed the presence of free formic and caprylic acids, the former being recognised by its qualitative reactions, and the latter by ignition of its silver salt; 0.0628 gram gave 0.0273 gram silver = 43.47%. The silver salt of caprylic acid requires = 43.02% Ag.

Determination of Phytosterols.—The oily portion remaining after removal of chlorophyll, free acids, phenol, esters, etc., soon solidified to a solid of butter-like consistency resembling Eudesmol. It was treated with petroleum ether (B. Pt. below 60°) which permitted the separation of a white solid. This constituent on re-crystallisation was resolved into various fractions, melting at 170°, 166°, 150° and 142°. An average sample purified from alcohol melted at 162°. It was distinguished by the magnificent magenta colour given when a drop of sulphuric acid was added to its solution in chloroform and acetic anhydride. It was found to be optically active.

0.0723 gram in 10 c.c. chloroform gave a mean reading of $+0.44^{\circ}$, $[a]_{\rm D}^{20^{\circ}}$, $+60^{\circ}$.

A molecular weight determination by the boiling point method gave the following result:—

0.6088 gram in 23 e.e. acetone elevated the boiling point 0.15° . M.Wt. = 395. $C_{27}H_{46}O$ requires 390.

The combustion results, although not quite so good, yet pointed to a molecular formula of $C_{27}H_{46}O$. The acetate was prepared, but it melted indefinitely between 120-130°, the quantity being too small for rigorous purification.

Determination of Essential Oil.—The portion of essential oil obtained from 40 grams of the Concrete Otto measured 8 c.c., and on distillation at 2-3 mm. behaved as follows:—

1st drops 80° collected 80-120° 1 c.c. and 120-140° 6 c.c.

The latter had $d_{\frac{1}{5}}^{\frac{5}{5}}$, 0.8743; a_{-D}^{30} ; n_{D}^{200} , 1.4716.

On further distillation a fraction of 3 c.c. was obtained, boiling at 125-129° at 3 mm. and possessing—

$$d_{\frac{1}{1}\frac{5}{5}}^{\circ} \ 0\cdot 8845, \ a_{\scriptscriptstyle \mathrm{D}}\text{--}1\cdot 2^{\circ}, \ n_{\scriptscriptstyle \mathrm{D}}^{20\circ} \ 1\cdot 4738.$$

A second preparation yielded 4 c.c., distilling at $130\text{-}150^{\circ}$ at 10 mm., having —

$$d_{\frac{15}{5}}^{\circ}$$
 0.8807, $a_{\rm D}$ -6°, $n_{\rm D}^{20}$, 1.4726.

A third preparation gave the following results:-

	Volume.	d 15° 15	a D	n 20°
130-133° 4–5 mm	2 e.e.	0.8763	$-2\cdot 2^{\circ}$	1 · 4695
133-153° 4–5 mm	2 c.c.	0.8618	-2·0°	1.4650

None of the fractions referred to reacted with phenylisocyanate, napthylisocyanate or phthalic anhydride. They appeared to be mixtures of high boiling alcohols with ketones. The molecular weights of the various fractions varied from 189 to 200. The combustion results were of little value but they pointed to the presence of an alcohol of 12 carbon atoms, and no evidence could be obtained with the small quantities available as to whether the principal fractions represented a chemical entity.

When the Concrete Otto, as received, was treated with aqueous potash solution as in the isolation of low boiling alcohols, free and combined, it was found that the volatile oil which came over differed somewhat from that obtained during treatment with alcoholic potash solution, as will be observed from the following results:—

Lot
$$26/10/26$$
 22 grams crude Otto yielded $2\frac{1}{2}$ c.c. of oil. $d\frac{15}{15}^{\circ}$ 0·9071, $a_{\rm D}$ -8·8°, $n_{\rm D}^{20}$ 1·4840

Lot
$$10/2/27$$
 20 grams crude Otto yielded $1\frac{1}{2}$ c.c. of oil. $d\frac{15}{5}$ ° 0·8861, $a_{\rm D}$ -1·6°, $n_{\rm D}$ 1·4804

Determination of β -Ionone.—The highest boiling fractions of the volatile oils possessed a pronounced but characteristic odour of β -Ionone, and these on treatment with semicarbazide hydrochloride and sodium acetate solutions yielded a crystalline derivative. This resembled in general physical characters the semicarbazone of β -Ionone, and moreover melted at 145--146°. The semicarbazone of a commercial sample of β -Ionone was prepared, and this on purification from ethyl alcohol melted at 148-149°.

A mixed melting point determination made with a mixture of the two specimens showed no depression. The presence of this ketone requires confirmation as I have been unable to trace any record of its previous occurrence in nature.

Determination of Ethyl Alcohol.—Apart from a small quantity of ethyl alcohol occurring as formate, about 5% of this alcohol was separated from the Concrete Otto by washing with warm water. It was identified by the Iodoform reaction and oxidation to acetic acid by means of potassium permanganate solution.

0.2130 gram of silver salt gave 0.1373 gram silver = 64.46% Ag.

The silver salt of acetic acid requires 64.67 % Ag.

Since the manufacturers have assured me that this alcohol is not used in the preparation of the Concrete Otto, it must, therefore, be naturally, occurring.

In conclusion, my thanks are due to Mr. F. R. Morrison, F.C.S., A.A.C.I. Assistant Economic Chemist, for much assistance in this investigation.